PLANETARY RESEARCH EXPL

How could life begin from a swirling chaos? How did Earth and its moon form? What can lunar rocks from the Apollo missions reveal? And what will scientists learn from exploration on distant moons? These questions are addressed in this four-part feature article on Lawrence Livermore's space science research.

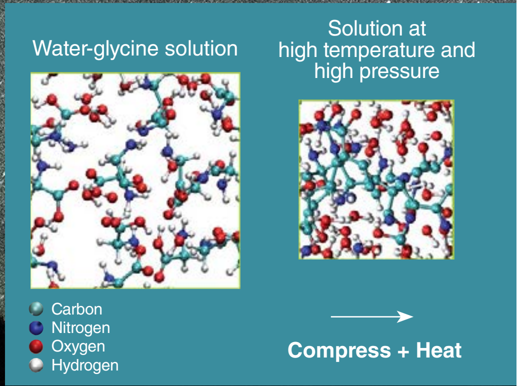
SHOCKING START TO LIFE

EARTH coalesced from a protoplanetary disk of gas, dust, and aggregations of particles about 4.5 billion years ago. Primordial Earth was a hostile place—volcanism, extreme heat, a turbulent atmosphere, intense ultraviolet radiation from a young, hot sun, and continual bombardment from comets and meteorites. How could such unwelcome conditions lead to a prebiotic chemistry that gave way to proteins, lipids, and other biomolecules between 3.5 and 4 billion years ago?

Researchers at Lawrence Livermore are exploring an unexpected pathway to the organic precursors of early biomolecules—precursors that originate with the impacts of astrophysical bodies on Earth. Comets, made mostly of water, ice, and dust, have been known since the 1970s to also contain a number of small molecules such as ammonia (NH_3) and methanol (CH_3OH). In 2009, the comet Wild II (pronounced "vilt 2") was found to contain glycine, the simplest protein-forming amino acid. The impact of comets provides abundant energy to drive chemical reactions that could produce a wide array of organic chemicals that are the building blocks of biomolecules.

Nir Goldman, a computational chemist and deputy group leader of the Non-Equilibrium Theory Group in the Laboratory's Materials Science Division, leads research that uses Livermore's high-performance computing (HPC) capabilities to simulate the chemistry that takes place when comets and other icy materials bearing organic chemicals collide with Earth. Goldman and his team build on an earlier study, funded by Livermore's Laboratory Directed Research and Development (LDRD) Program, of shock-compressed materials to determine whether prebiotic compounds such as amino acids might emerge under high temperatures and pressures.

"Experiments to recreate such conditions are extremely challenging due to the large number of interconnected variables at play," says Goldman. "Factors include the composition of the initial material to be studied and the peak conditions achieved during shock compression. Analyzing the products after the shock process is one of the biggest challenges. A plethora of reactions can take place, and contamination from biological sources—for example, a researcher's hands—is extremely easy."

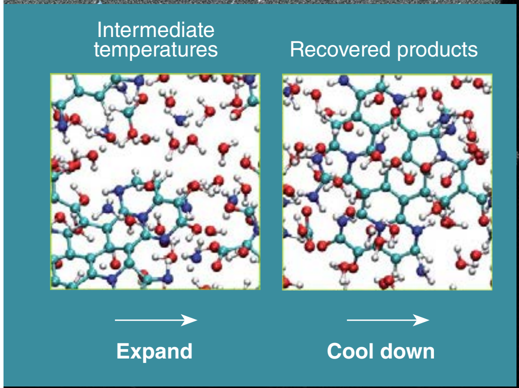


In a simulation designed to show the effects of cometary impact, a water-glycine mix is compressed and heated, then expanded and cooled, yielding life-building hydrocarbons.

Simulating Shock

To help direct experimental shock compression efforts, Goldman and his colleagues performed quantum mechanical simulations of prebiotic shock synthesis to explore what happens chemically under impact conditions of a comet. After setting up initial conditions including pressure and temperature, initial mix of chemicals, strain rates, and other parameters, the simulations modeled comet impact conditions at the atomistic level while accurately describing the dynamic breaking and forming of chemical bonds. In this case, their simulations spanned more than 50 gigapascals (GPa)—nearly 500,000 times Earth's atmosphere—and temperatures up to 5,000 kelvin. "The real art of these simulations is the judicious choice of setting these boundary conditions

ORING OUR PAST AND FUTURE



to mimic the conditions you want," says staff scientist and computational chemist Matthew Kroonblawd, a member of Goldman's team.

To their surprise, simple mixtures containing water, small organic compounds, and ammonia yielded amino acids and a number of other potentially life-building compounds when subjected to these intense conditions. Later, confirming experiments were performed using a light gas-gun facility at the University of Kent. An aqueous mixture of similar composition was subjected to an impact shock of more than 50 GPa, and researchers identified a large variety of amino acids in the post-shock ice mixture.

A follow up study in 2019 by Kroonblawd, Goldman, and Livermore's Rebecca Lindsey reported the results of simulating a mix of glycine and water under impact scenarios including cooling and equilibrating to ambient conditions. In this case, carbon-rich structures condense under high pressures and temperatures and subsequently unfold into nitrogen-containing polycyclic aromatic hydrocarbons (NPAHs) during fracture and cooling. NPAHs are important prebiotic precursors for synthesizing molecules that are the basis of complex proteins such as RNA and DNA.

Path to Prebiotic Compounds

Research published in 2020 by Brad Steele, Goldman, I-Feng "Will" Kuo, and Kroonblawd simulated a rotational diamond anvil cell experiment. Rotating diamond anvils apply a compressive shearing force to a small chamber containing a glycine mixture. A modeled compressive shear stress of 10 GPa produced a complex chemistry of prebiotic compounds including polypeptides, such as chains of amino acids that form the building blocks of proteins. These studies indicate that simple molecules like glycine support richly varied chemistry under extreme conditions. Other simulation studies from Goldman's group have generated long-chain carbon molecules, formaldehyde, and hydrogen-nitrogen-carbon-oxygen compounds such as hydrogen cyanide, which are building blocks of biomolecules. "We've run hundreds of simulations on Livermore's HPC facility to get good statistics," says Goldman. "This work is only possible here and only because of the Laboratory's supercomputers."

Now funded by NASA's Exobiology program, Goldman's group is undertaking a study of a heterogenous system to determine the possible shock synthesis of organophosphates (compounds containing phosphate ions) that are key components of biomolecules such as DNA, RNA, and adenosine triphosphate. The team's studies will include aqueous mixtures of the iron-phosphorus mineral schreibersite, a common component of meteorites that may have contributed as much as 10 percent of the phosphorus thought to be present in the crust of early Earth. Schreibersite could have acted as both a source of elemental phosphorus and as a catalyst for lowering energetic barriers for organic chemical reactivity. Extreme thermodynamic conditions can act as a driving factor in creating more complicated chemical compounds with carbon-phosphorus bonds. This latest study will give Goldman and his team a unique opportunity to explore the catalysis of potentially life-building compounds in aqueous environments and answer long-standing questions in astrobiology.

—Allan Chen

Livermore's Nir Goldman (left) and Matthew Kroonblawd modeled cometary bombardment conditions to understand the chemical bonds broken and formed after impact. (Photo by Garry McLeod.)

Key Words: amino acids, comet, glycine, meteorite, organophosphates, prebiotic molecules, rotational diamond anvil cell, schreibersite.

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READING COSMIC ROCKS

WHO would have guessed that rocks could tell us so much—not just about Earth's geological history, but about the evolution of our solar system, and its planets, moons, and asteroids? Laboratory researchers Lars Borg and Greg Brennecka don't have to guess. They know.

In their roles as cosmochemists, Borg and Brennecka read the clues embedded in extraterrestrial samples gathered during targeted space missions as well as the random meteorites sourced mainly from the solar system's primary repository of history, the asteroid belt. Insights into the events that took place billions of years ago can be gleaned from isotopic signatures in general. The ticking clocks of radioactive isotopes embedded in these rocky samples are particularly helpful. Event ages can be determined by measuring specific elemental and isotopic ratios in a sample, and these ratios can reveal the age and origin of a sample, and importantly, the sequence and timing of events in the solar system. (See the box on p. 7.)

Investigations by the Livermore team cover a wide swath of time and space. Brennecka focuses on the earliest history of the solar system, the first 5 million or so years after the Sun ignited and the first solids formed. Borg, on the other hand, focuses on the evolution of satellites and planets such as the Moon, Mars, and Earth. Brennecka notes that their areas of interest overlap and reinforce each other. "As the Sun was gathering mass and igniting, the first solids in the solar system formed, followed by the accretion and differentiation of early protoplanets," he says. "These events determined the evolutionary course of our solar system and the planetary bodies within it."

Origin Stories

In 2010, the two researchers first teamed up to use Livermore-developed techniques to evaluate isotopic signatures in calcium aluminum–rich inclusions (CAIs) from the Allende meteorite that landed in Mexico in 1969. These CAIs were the earliest solids to form in our solar system, predating the terrestrial planets by more than a million years. The resultant isotopic signatures provided evidence indicating that the cloud of matter condensing to form the Sun and planets was showered with material produced by a nearby supernova explosion. (See *S&TR*, July/August 2014, pp. 12–14.)

Borg has turned a cosmochemist's eye upon the mystery of the Moon's origin as well. In one theory, the Moon formed at the same time as the Earth, accreting from a primordial cloud of gas and dust, making the Moon around 4.5 billion years old. Original isotopic analyses on samples gathered during the Apollo missions, which ran from 1969 to 1972, varied widely, suggesting the Moon could be between 4.32 billion to 4.56 billion years old. Beginning in the late 1990s, a team headed by Borg took another look at the samples using more modern techniques and equipment. It turned out that, no matter where the samples had been collected and what isotopic clocks were used, the rocks all told of a formation between 4.33 and 4.38 billion years ago, pointing to a much younger Moon. These Livermore analyses gave weight to the "Giant Impact" theory, in which a large body, approximately the size of Mars, smashed into early Earth. Superheated rock and dust hurtled into space, where, with the help of gravity, it eventually accreted, forming the Moon. (See *S&TR*, September 2017, pp. 12–15.)

Lars Borg (left) and Greg Brennecka prepare lunar samples for isotopic measurement to study the chronology of the Moon. (Photo by Garry McLeod.)

In more recent projects, including Borg's work with Livermore's Thomas Kruijer, Josh Wimpenny, and Corliss Sio, researchers have turned to isotopic analysis to pin down when Mars' "magma ocean" began to solidify into the planet's mantle. Thermal models predicted this solidification would have started less than 1 million years after the formation of the planet's core. To test this, the team applied the ^{53}Mn–^{53}Cr radiochronometer, a decay system where manganese-53 (half-life of approximately 3.7 million years) decays to chromium-53, to Martian meteorites. Results demonstrated this chronometer was not "alive" when Mars formed its mantle and crust, indicating that the magma ocean solidified at least 25 million years after the beginning of the solar system—at least 20 million years after the core is thought to have formed. One possible explanation, notes Borg, could be that early Mars sported a dense atmosphere that acted as an insulator keeping the magma ocean from solidifying.

Creating Timetables

The most exciting element of cosmochronology research, according to Brennecka, is learning how every facet links together. "Through examining a variety of samples, we can build a picture of not only how the planets form and evolve, but how the solar system came into being," he says. "The Laboratory enables this groundbreaking cosmochemistry work by having the best analytical capabilities and equipment to measure isotopic ratios. I can't think of any other place that has such an assortment of capabilities under one roof."

Work funded by Livermore's Laboratory Directed Research and Development (LDRD) Program united Brennecka and postdoc Jan Render to measure the isotopic signatures of neodymium and zirconium in samples of meteorites from the asteroid belt. Because many planets are not positioned where they originally formed, particularly the giant planets, these measurements of asteroid belt material determined where these samples initially formed, helping create a broad reconstruction of the primordial solar system.

Livermore's cosmochemists also serve with a team analyzing recently opened core samples gathered on the Moon in 1972, during the last Apollo mission. This work is focused on chronology of previously unexamined samples and serves to gather information on the behavior of volatile elements on the Moon and Earth.

Borg, who has been named to the National Academy of Science's Planetary Science and Astrobiology Decadal Survey steering committee, notes that this research effort positions the Laboratory for conducting forensic analyses of samples from future Moon missions. "Livermore has a seat at the table when the academy assesses key scientific questions in planetary science and astrobiology and identifies missions and initiatives for the decade 2023–2032," says Borg. Other sample-collection missions include the Mars Sample Return Campaign, scheduled to launch in 2026, and the OSIRIS-REx mission, set to return asteroid samples in 2023. In addition, large quantities of lunar samples from many new areas of the Moon are expected to be returned when NASA's ARTEMIS manned space flight program matures in the near future. "We have become a one-stop shop for extraterrestrial geochronological analysis and there are some fantastic sample analysis opportunities ahead," says Borg. "It's an exciting time to be in the field and at Lawrence Livermore."

—Ann Parker

A Storied History of Isotopic Analysis

The Laboratory has long been in the business of studying isotopes. Early on, its radiochemists conducted isotopic analyses for atmospheric and underground nuclear tests; today, nuclear forensics plays a key role in the Laboratory's security missions. (See *S&TR*, April/May 2018, pp. 4–11 and *S&TR*, October/November 2014, pp. 12–18.) Livermore's Lars Borg sees only a short step from applying isotopic research to nuclear forensics to answering questions of cosmochemical importance. "Planetary materials undergo processes that are relevant to nuclear forensics, such as nuclear decay, neutron capture, and spallation," he says. "Additionally, the elements of interest to cosmochemistry have multiple isotopes of interest for forensic purposes. Finally, the analytical techniques are essentially identical for both applications." Noting important differences, Borg points out that the magnitude of isotopic effects can be much more muted in natural samples, requiring precision measurements to identify extremely small isotopic differences between samples of very little mass. In many cases, the procedures the Laboratory develops to answer a cosmochemical question, such as determining the nucleosynthetic sources for the elements in a meteorite sample, can also be used in nuclear forensics and other mission-critical work.

Key Words: Allende meteorite, Apollo mission, asteroid, cosmochemistry, extraterrestrial geochronology, Giant Impact, isotope analysis, isotopic signature, Laboratory Directed Research and Development (LDRD) Program, Moon, Mars, meteorite, NASA, solar system.

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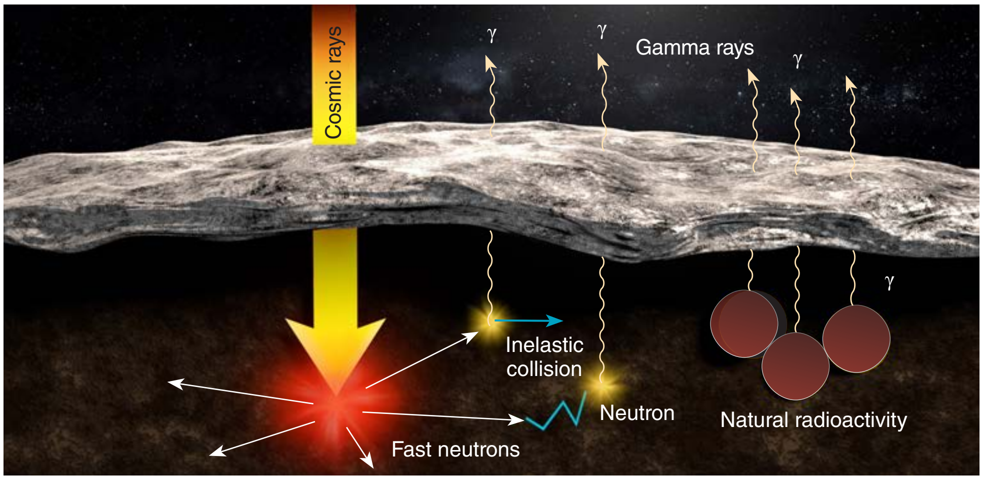
GAMMA RAY EYES ON DISTANT MOONS

GAMMA RAYS—high-energy electromagnetic waves produced by the decay of radioactive isotopes—are found in the depths of space and on the surface of planets, planetoids, and moons. In space, neutron stars, pulsars, and supernova explosions emit gamma rays. On planets, cosmic ray bombardment and the less dramatic process of radioactive decay produce gamma rays. Lightning and nuclear explosions on Earth yield them as well.

Since gamma–ray emission provides a unique fingerprint of a radioactive material's isotopic composition, the Laboratory has long been in the business of designing and fielding gamma-ray spectrometers. Used in national security, the devices locate radioactive materials at shipping ports and border crossings. As nuclear safeguards, they identify and quantify the isotopes in nuclear processing facilities.

Lawrence Livermore is also recognized for its development of germanium-based gamma-ray spectrometers for planetary exploration. The high-purity germanium crystals in these detectors provide excellent resolution at −180°C, a requirement that presents its own challenges when journeys take years and temperatures are extreme. Germanium-based gamma-ray detectors developed by Livermore's Morgan Burks, Geon-Bo Kim, and Nathan Hines will be part of deep-space missions to the asteroid Psyche-16 (launch date 2022), the two moons of Mars (2024), and Saturn's moon Titan (2027). The Livermore team collaborates with Johns Hopkins University Applied Physics Laboratory (APL) researchers, who integrate the gamma-ray detectors with other instrumentation and deliver the final systems to NASA.



When high-energy cosmic rays bombard an airless planetary surface, gamma rays are emitted through processes such as inelastic collision and neutron capture. Gamma rays can also be emitted from naturally occurring radioactive materials such as thorium, potassium, and uranium on the planetary surface. The GeMini-Plus will measure the energy of the gamma rays with high resolution, helping scientists to identify the asteroid's composition. (Rendering by Veronica Chen.)

An Established Collaboration

This effort isn't the "first rodeo" for the Livermore-APL collaboration. About 20 years ago, Livermore and APL developed a lightweight, germanium-based gamma-ray spectrometer for NASA's MESSENGER mission to Mercury (See *S&TR*, June 2005, p. 23–24.) The venture provided new insights, causing researchers to reconsider theories on Mercury's formation. That instrument led to the GeMini, a germanium (Ge)-based spectrometer with an ultraminiature electromechanical cooling system (Mini). Low power, low mass, low weight, and rugged, the R&D100 Award–winning GeMini was small enough to hold in the palm of one hand. (See *S&TR*, October/November 2009, pp. 8–9.)

The GeMini gave way to the versatile GeMini-Plus, which sports an improved, simplified, and more rugged design. The team recently delivered the GeMini-Plus for the mission to Psyche-16, located in the asteroid belt between Mars and Jupiter. Psyche is composed largely of iron, unlike most asteroids, which are mostly rock. "Psyche is thought to be a planetary core, a remnant of a collision during the early stages of the development of the solar system," says Burks. Data gathered by the GeMini-Plus on the elemental composition of Psyche's surface could provide insights into the cores of our solar system's "inner" planets—Earth, Mars, Mercury, and Venus—and into planetary evolution and formation. (See *S&TR*, May 2019, pp. 17–19.)

(From left to right) Livermore's Geon-Bo Kim, Nathan Hines, and Morgan Burks designed the GeMini-Plus, a high-resolution gamma-ray spectrometer that will be part of the NASA mission to the Psyche asteroid. The team is creating similar detectors for missions to the moons of Mars and to Saturn's moon, Titan. (Photo by Garry McLeod.)

Outfitting New Instrumentation

A modified GeMini-Plus will be incorporated into NASA's Mars-Moon Exploration with Gamma rays and Neutrons (MEGANE) instrument, which will use gamma-ray and neutron spectroscopy to measure the elemental composition of the two Mars moons, Phobos and Deimos. MEGANE is one of eleven instruments slated for the Japan Aerospace Exploration Agency's Martian Moons Explorer (MMX). "Our spectrometer may help answer some fundamental questions about how Mars's moons were formed," says Burks. "Are they captured asteroids? Remnants of a big impact on Mars? Or, accreted leftover material from Mars's formation? We hope to find out." After conducting remote-sensing measurements of both moons, the MMX will land on the surface of Phobos, grab a sample of its moon dust, and fly back to Earth. The round-trip mission is expected to take about five years.

While engineering the spectrometer for MEGANE/MMX, the team is also hard at work on the instrument for the Dragonfly mission. Part of NASA's New Frontiers program, Dragonfly will search for the building blocks of life on Saturn's largest moon, Titan. The eight-bladed rotorcraft will maneuver like a large drone, zooming about the icy moon's surface, landing to take samples, and taking off again. Livermore's gamma-ray detector will measure the elemental composition of the landing sites, helping with site characterization and sample selection. "Titan has a dense, nitrogen-based atmosphere along with methane clouds and rain," Burks notes. "The surface has liquids, ammonia ices, and complex organic molecules, which could be precursor molecules to life."

In addition to preparing detectors for these missions, Burks and his team are also involved in a project funded by the Laboratory Directed Research and Development Program to develop a science capability that complements the Laboratory's space-based hardware competencies. Burks explains, "The Laboratory is now viewed as an expert in delivering gamma-ray spectroscopy instrumentation for space exploration. That expertise and our competencies in nuclear science put us in an excellent position to contribute to nuclear planetary science and aid in transferring the technology we've developed for space applications to the next-generation of terrestrial search instruments."

—Ann Parker

Key Words: asteroid belt, detector, Dragonfly, gamma-ray spectrometry, GeMini-Plus, germanium (Ge)-based spectrometer, Japan Aerospace Exploration Agency, Johns Hopkins University Applied Physics Laboratory (APL), Mars-Moon Exploration with Gamma rays and Neutrons (MEGANE), Martian Moons Explorer (MMX), MESSENGER, NASA, New Frontiers program, Phobos, Psyche-16, Saturn, Titan.

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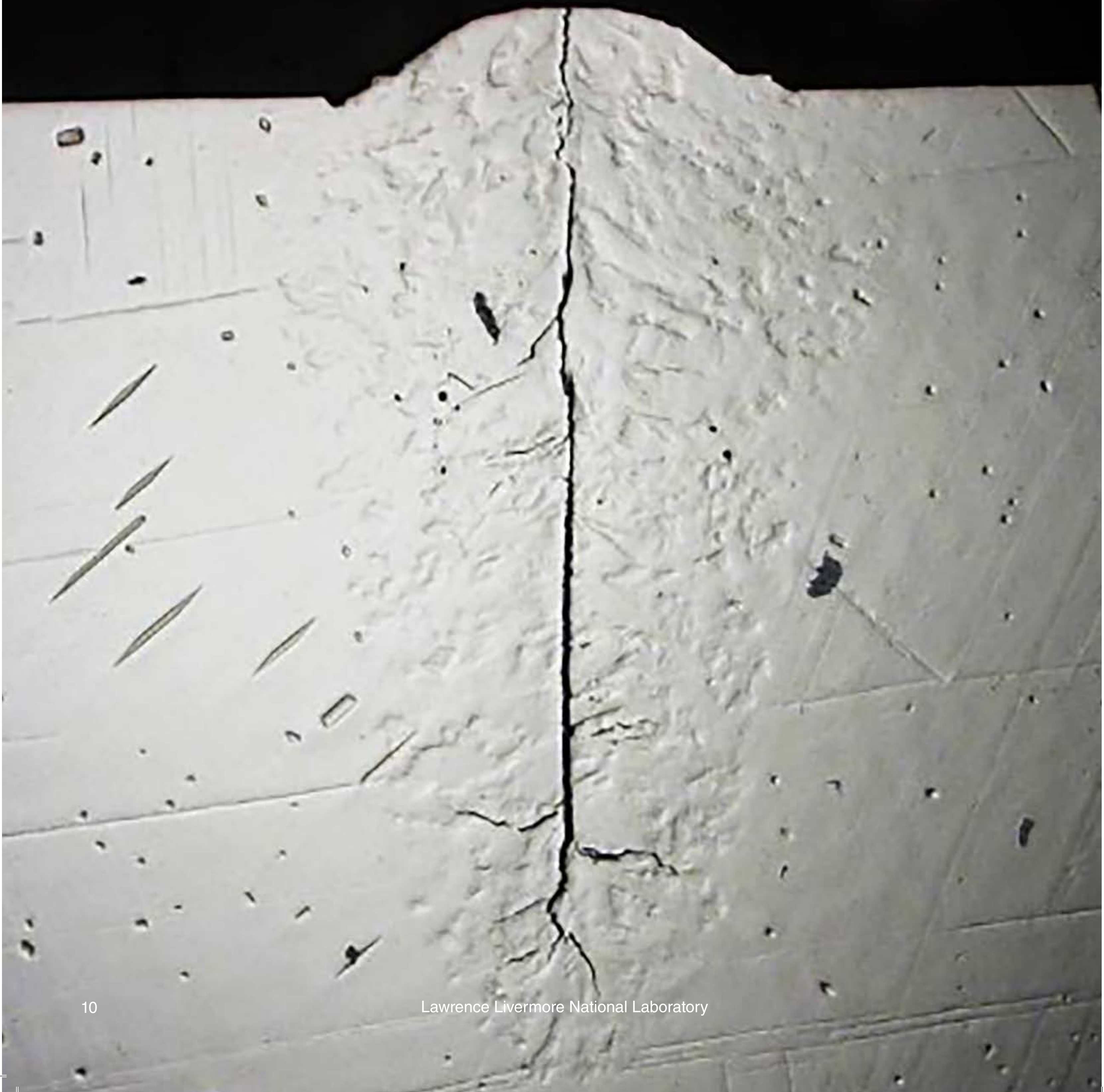
WELDING WITH ASTEROIDS?



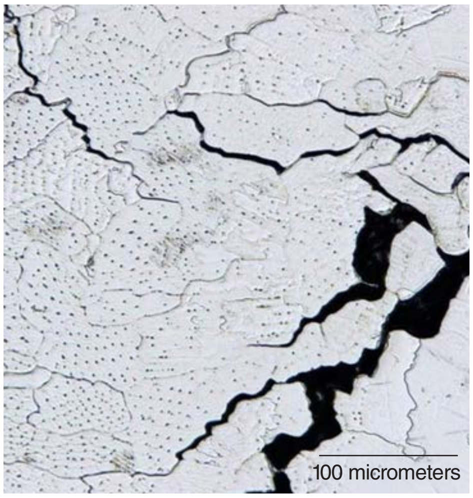
NEWS articles and media outlets regularly buzz with opinions and progress on the future of establishing colonies in space and on the Moon and Mars. Such possibilities, once the stuff of science fiction, are now on the way to becoming science fact. These endeavors will require building and maintaining structures for transportation and habitation.

For off-Earth structures, space adventurers will most likely need materials at hand for fabrication and repairs. Lawrence Livermore materials scientist John Elmer explains, “Transporting large amounts of traditional building materials such as aluminum, titanium, and stainless steel from Earth into space is expensive. Materials for space construction and repairs will most likely come from the Moon, asteroids, or meteorites.” Asteroids—large “rocks” orbiting the Sun—and meteorites—asteroids that crash onto planets or moons—often have a high percentage of iron and nickel, two important elements of stainless steel and low expansion, Invar alloys. “People have suggested that perhaps these metal-rich objects could be used for extraterrestrial construction,” says Elmer.

Key to construction is the capability to weld. In the 1970s, experiments on NASA’s Skylab space station proved the feasibility of electron-beam welding steel in space, where conditions are ideal since the welding technique requires a vacuum to operate. However, the Skylab experiments used high-quality steel that had been refined on Earth to the proper chemistry for welding. Would the same technique work on extraterrestrial material that was rich in iron, the primary element of steel? Elmer decided to find out.

Meteorite Fragments Put to the Test

Elmer rounded up a team, including Livermore’s Gordon Gibbs, Lenny Summers, Gil Gallegos, Cheryl Evans, and James Embree, and obtained a 722-gram specimen of the Canyon Diablo meteorite, which plunged to Earth about 50,000 years ago, shattering and forming the 1.3–kilometer-diameter Meteor Crater in Arizona. Nearly 30 tons of fragments of this iron-and-nickel-rich meteorite have been collected, making samples available for research.



(opposite) An electron-beam weld in the iron–nickel meteorite displays a large centerline crack. (above) A magnified image of the weld fusion zone shows where phosphorous compounds resulted in cracks at the grain boundaries.

Specimens were electron-beam welded at the Laboratory in a vacuum similar to the vacuum of space. The welds were several millimeters deep, typical of those needed to join parts. However, the small welds cooled much more rapidly than meteorites. “An asteroid in space can take a hundred million years to solidify and cool from its initial formation, a cooling rate that cannot be replicated here on Earth where solidification and cooling take place in less than a minute,” Elmer explains. “I expected that the microstructures of our welds would be considerably different from that of the original meteorite, and they were.” The vastly different cooling rates in the laboratory environment combined with the presence of phosphorous, sulfur, and carbon-rich particles scattered throughout the meteorite led to cracks in the welds and a weak joint. “Our experiments showed that welding meteoritic iron in its native state has significant challenges that won’t be overcome by welding the same piece of metal over and over and hoping for the best,” says Elmer. “However, the challenges are not insurmountable. We just need a different approach.”

Refining Space Materials

One intriguing possibility, which Elmer described in a 2018 patent, would be to refine the asteroidal or meteoritical iron using existing elements known to be present on the Moon’s regolithic surface. The first step would be identifying an asteroid or meteorite with a high percentage of iron, mining it, and then metallurgically refining the material to remove impurities harmful to steel making and welding. Once refined, the material could be atomized into powder, facilitated by the low-gravity and vacuum of space. “This powder could be used to additively manufacture steel parts using conventional electron-beam or laser-beam 3D printing methods—welding-related processes that also require high-quality metal,” says Elmer. He adds that 3D printed parts could be welded together to create larger structures, as on Earth. In fact, the International Space Station and NASA demonstrated the feasibility of printing 3D parts in space in 2014.

Many challenges remain for doing this work using extraterrestrial iron. For instance, refining the metal requires significant amounts of energy, and electron-beam generation requires high voltage power supplies. “Still, it’s an intriguing proposition that makes metallurgical sense,” says Elmer. “With more innovative thought and experimentation, plus some creative, technical elbow grease, welding in space would become a reality.”

—Ann Parker

Key Words: additive manufacturing, asteroid, electron-beam welding, iron, Mars, materials science, meteorite, Moon, space, steel.

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